

Supporting information

Structural and Spectroscopic Investigation of Novel 2D and 3D Uranium Oxo-Silicates/Germanates and Some Statistical Aspects of Uranyl Coordination in Oxo-Salts

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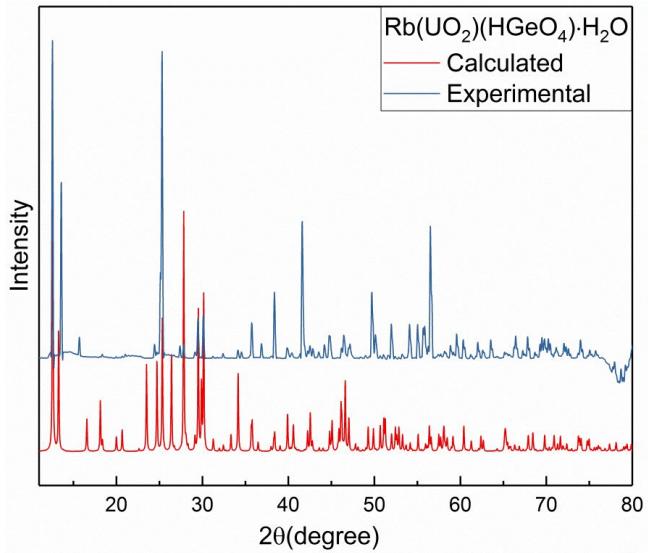


Figure S1(a). Powder diffraction pattern collected for the reaction product $\text{Rb}(\text{UO}_2)(\text{HGeO}_4)\cdot\text{H}_2\text{O}$. The comparison between Calculated (red) and Experimental (blue) PXRD patterns shows that the experimental data do not fully match the calculated PXRD. The other unidentified peaks may correspond to Rb_2UO_4 and UO_3 .

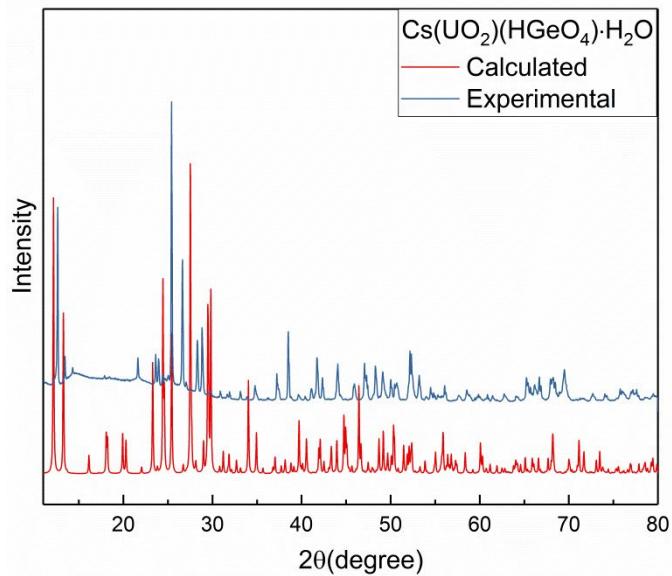


Figure S1(b). Powder diffraction pattern collected for the reaction product $\text{Cs}(\text{UO}_2)(\text{HGeO}_4)\cdot\text{H}_2\text{O}$. The comparison between Calculated (red) and Experimental (blue) PXRD patterns show that the experimental data has a big difference with the calculated PXRD, indicating the low yield of the phase. The other unidentified peaks correspond to UO_3 and Cs_2UO_4 .

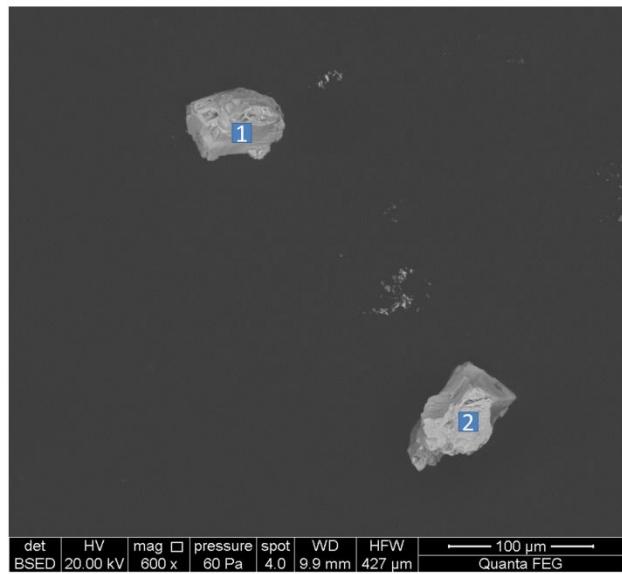


Figure S2(a). SEM-EDS result for $\text{K}_4(\text{UO}_2)_2\text{Si}_8\text{O}_{20}\cdot 4\text{H}_2\text{O}$.

Table S1 (a). Atom ratio of $\text{K}_4(\text{UO}_2)_2\text{Si}_8\text{O}_{20}\cdot 4\text{H}_2\text{O}$. (U is normalized as 2)

	U	Si	K
Point1	2	9.71	4.91
Point2	2	10.24	4.33
Average	2	9.98	4.62

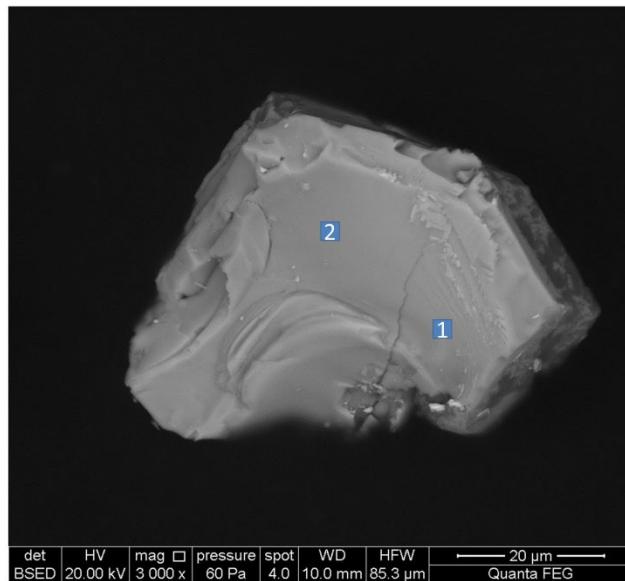


Figure S2(b). SEM-EDS result for $\beta\text{-K}_2(\text{UO}_2)\text{Si}_4\text{O}_{10}$.

Table S1 (b). Atom ratio of $\beta\text{-K}_2(\text{UO}_2)\text{Si}_4\text{O}_{10}$. (U is normalized as 1)

	U	Si	K
Point1	1	3.31	2.41
Point2	1	3.93	2.47
Average	1	3.62	2.44

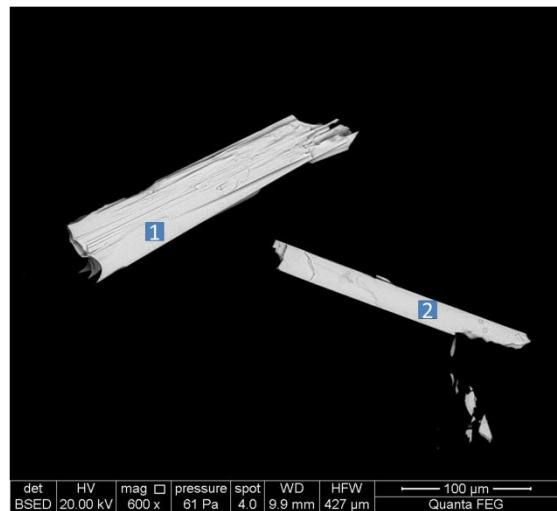


Figure S2(c). SEM-EDS results for $\text{Na}_6(\text{UO}_2)_3(\text{Si}_2\text{O}_7)_2$.

Table S1 (c). Atom ratio of $\text{Na}_6(\text{UO}_2)_3(\text{Si}_2\text{O}_7)_2$. (U is normalized as 3)

	U	Si	Na
Point 1	3	5.15	6.32
Point 2	3	4.87	5.31
Average	3	5.01	5.82

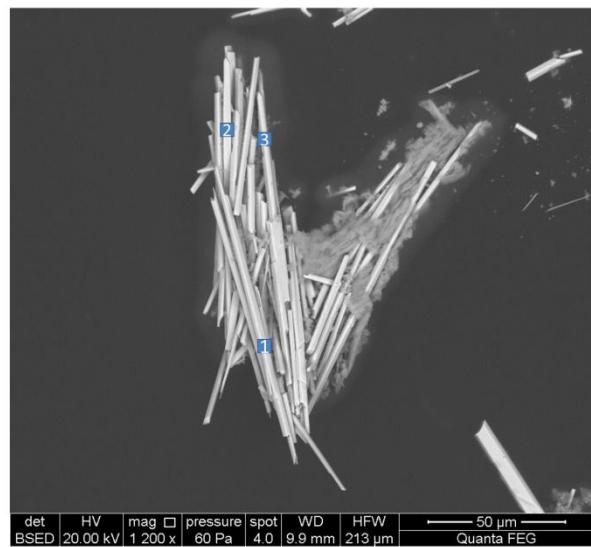


Figure S2(d). SEM-EDS result for $\text{Rb}(\text{UO}_2)(\text{HGeO}_4)\cdot\text{H}_2\text{O}$.

Table S1 (d). Atom ratio of $\text{Rb}(\text{UO}_2)(\text{HGeO}_4)\cdot\text{H}_2\text{O}$. (U is normalized as 1)

	U	Ge	Rb
Point 1	1	1.12	1.17
Point 2	1	1.32	0.94
Point 3	1	1.07	1.09
Average	1	1.17	1.07

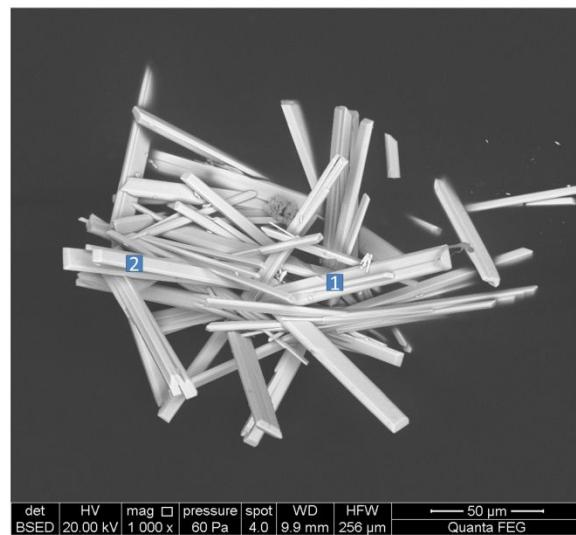


Figure S2(e). SEM-EDS result for $\text{Cs}(\text{UO}_2)(\text{HGeO}_4) \cdot \text{H}_2\text{O}$.

Table S1 (e). Atom ratio of $\text{Cs}(\text{UO}_2)(\text{HGeO}_4) \cdot \text{H}_2\text{O}$. (U is normalized as 1)

	U	Ge	Cs
Point1	1	1.23	1.09
Point2	1	1.09	1.10
Average	1	1.16	1.10

Table S2. Bond valence calculation results for β -K₂(UO₂)Si₄O₁₀, and A(UO₂)(HGeO₄)·H₂O (A = Rb, Cs), respectively. Note that for an atom, the corresponding valence V is obtained through the following formula:

$$V = \sum_i \exp [-(R_i - d_i)/b]$$

Here the bond valence parameter R_i and constant b of hexavalent U are taken from Burns et al.¹ The bond valence parameter R_i and constant b of the other elements are provided by Brese and O'Keeffe.^{2,3}

(a) BVS calculation for β -K₂(UO₂)Si₄O₁₀.

	U	Si(1)	Si(2)	K	Σ
O(1)	1.8008 ^{2↓}			2.7787	1.9345
				2.8303	
O(2)	2.2319 ^{2↓}		1.573	2.8457	1.9793
O(3)	2.2469 ^{2↓}	1.5635		2.8526	2.0639
				3.0763	
O(4)		1.6106	1.6245	3.0942	2.1094
O(5)		1.5902			2.1913
O(6)		1.5811	1.6111		2.1587
O(7)			1.5815	3.3151	2.3247
Σ	5.9293	4.4331	4.3036	0.8022	

(b) BVS calculation for $\text{Cs}(\text{UO}_2)(\text{HGeO}_4)\cdot\text{H}_2\text{O}$.

	U	Ge	Cs	Σ
O(1)	1.7791		3.0362	2.0247
			3.1048	
O(2)	2.3497	1.7543	3.3999	2.0189
		2.4795		
O(3)	1.7716		2.9037	2.164
			3.0327	
O(4)	2.3084	1.7855		1.914
		2.481		
O(5)	2.2769	1.6799	3.702	1.862
O(6)		1.7961	3.5612	1.041
			3.2107	
OW(1)			3.1317	0.205
			3.4588	
Σ	5.993	3.967	1.270	

(c) BVS calculation for Rb(UO₂)(HGeO₄)·H₂O.

	U	Ge	Rb	Σ
O(1)	1.7747		2.9044	2.009
			3.0013	
O(2)	2.3197	1.7882	3.2549	1.953
		2.4938		
O(3)	1.787		2.7556	2.088
			2.921	
O(4)	2.3299	1.7688		1.930
		2.4826		
O(5)	2.3055	1.6364		1.946
O(6)		1.8289	3.1335	0.926
			3.5968	
OW(1)			3.0395	0.196
			3.2297	
Σ	5.917	3.998	1.132	

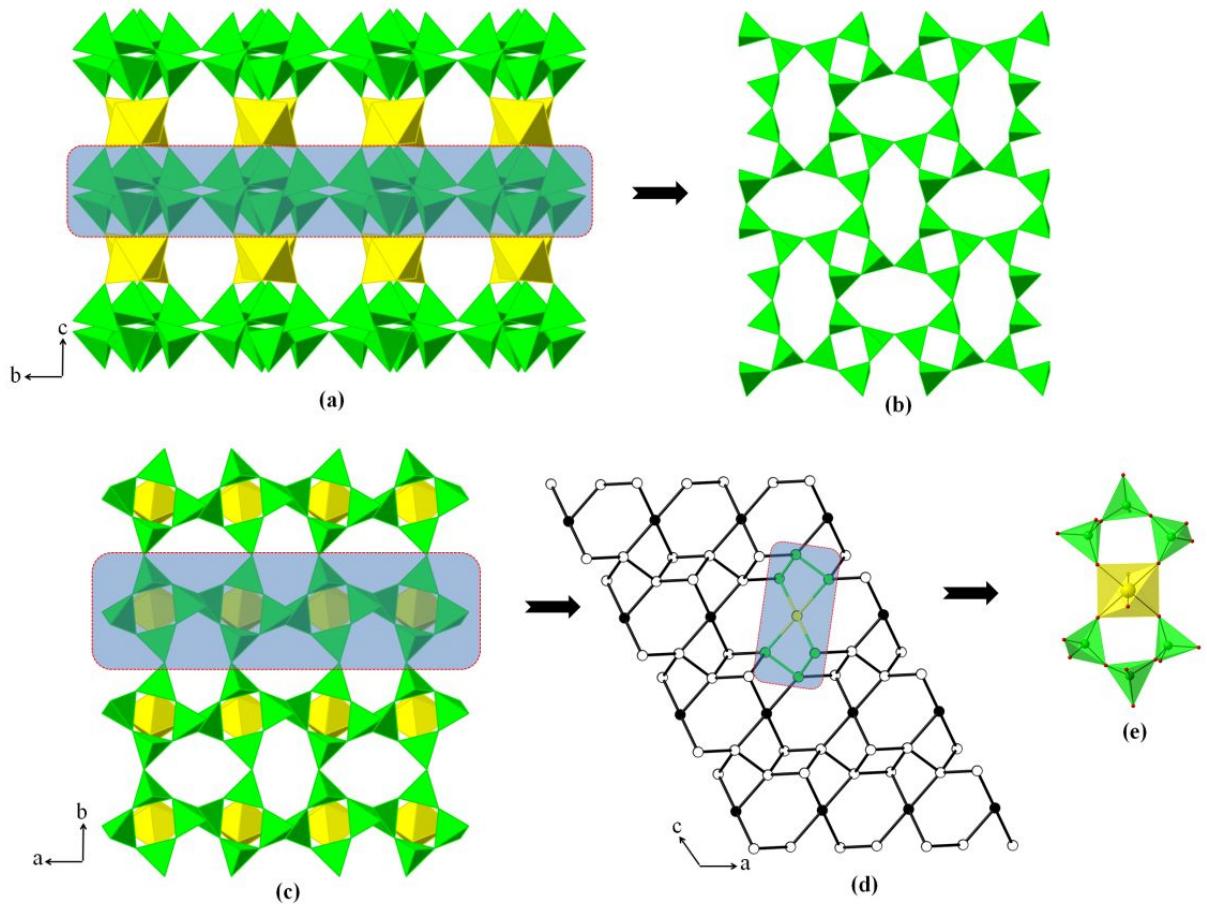


Figure S3. (a,c) The structure of $\text{Na}_2(\text{UO}_2)(\text{Si}_4\text{O}_{10}) \cdot 2.1\text{H}_2\text{O}$ viewed along the $[100]$ and $[100]$ directions. (b) Silicate layer with 4- and 8-membered rings in the compound. (d) Topology of a slab in the $\text{Na}_2(\text{UO}_2)(\text{Si}_4\text{O}_{10}) \cdot 2.1\text{H}_2\text{O}$ constructed from SBUs $[\text{UGe}_6]$ heptamers (**1+A+1 Type**) by edging-sharing. Key: yellow tetragonal bipyramids, UO_6 ; green tetrahedra, SiO_4 .

Table S3. Statistical results of coordination environments of uranyl ions for all known uranyl anion oxo-compounds, and the ionic potential of central cations in oxo-anions.

Compounds	Coordination number (CN) of U						Average of CN	Central cations	Radius of central cations (pm)	Electric charge of the cation (e)	Ionic potential (IP) (e/pm)	Average of IP (e/pm)
	4	5	6	4-, 5-, 4-,	5-, 6- 5-,	6-						
U-B ³⁺ -O	7	16	5	1	1	5.32	B +3	27		3	0.111	0.111
U-Si/Ge ⁴⁺ -O	30	28				4.48	Si +4	40		4	0.1	0.088
							Ge +4	53		4	0.075	
U-P/As ⁵⁺ -O	40	40	14	11	14	4	4.85	P +5	38	5	0.132	0.120
								As +5	46	5	0.109	
U-S/Se/Te ⁶⁺ -O	4	76	1			4.96	S +6	29		6	0.207	0.152
							Se +6	42		6	0.143	
							Te +6	56		6	0.107	
U-Cr/Mo/W ⁶⁺ -O	5	55	2			4.95	Cr +6	44		6	0.136	0.113
							Mo +6	59		6	0.102	
							W +6	60		6	0.10	
U-P/As ³⁺ -O	1	10	1	2		4.88	P +3	44		3	0.068	0.06
							As +3	58		3	0.051	
U-Se/Te ⁴⁺ -O	5	17	3	3	7	5.04	Se +4	50		4	0.08	0.061
							Te +4	97		4	0.041	

Table S4. Raman shift (cm^{-1}) and proposed band assignments in the range of 100 – 1200 cm^{-1} for $\text{K}_4(\text{UO}_2)_2\text{Si}_8\text{O}_{20}\cdot 4\text{H}_2\text{O}$, β - $\text{K}_2(\text{UO}_2)\text{Si}_4\text{O}_{10}$ and $\text{Na}_6(\text{UO}_2)_3(\text{Si}_2\text{O}_7)_2$, respectively.

$\text{K}_4(\text{UO}_2)_2\text{Si}_8\text{O}_{20}\cdot 4\text{H}_2\text{O}$	β - $\text{K}_2(\text{UO}_2)\text{Si}_4\text{O}_{10}$	$\text{Na}_6(\text{UO}_2)_3(\text{Si}_2\text{O}_7)_2$	Assignments	Ref.
179	115, 173	130, 185	Mixing modes	4
223, 297	217, 275, 294, 345	232, 276, 362	$\nu_2 (\text{UO}_2)^{2+}$	5
403			$\nu_3 (\text{SiO}_4)^{4-}$	6, 7
429, 467, 492	439, 478	487	$\nu_1 (\text{Si}-\text{O}-\text{Si})$	8
520			$\nu_1 (\text{Si}-\text{O}-\text{Si})$	8, 9
576	560		$\nu_4 (\text{SiO}_4)^{4-}$	6, 10
605, 656			$\nu_4 (\text{SiO}_4)^{4-}$	6, 10
	686	679	$\nu_1 (\text{Si}-\text{O}-\text{Si})$	11
751,	762	719, 742, 761	$\nu_1 (\text{UO}_2)^{2+}$	6, 7
781	779		$\nu_1 (\text{U}-\text{O bonds})$	6
813		827, 898, 924	$\nu_3 (\text{UO}_2)^{2+}$	6, 12
952, 961	959, 981		$\nu_1 (\text{SiO}_4)^{4-}$	6, 13
1091	1078	1026	$\nu_3 (\text{SiO}_4)^{4-}$	10

* ν_1 – symmetric stretching vibrations; ν_2 – symmetric bending vibrations; ν_3 – antisymmetric stretching vibrations; ν_4 – out-of-plane bending vibrations.

Table S5. Raman shift (cm^{-1}) and proposed band assignments in the range of 100 – 4000 cm^{-1} for $\text{A}(\text{UO}_2)(\text{HGeO}_4) \cdot \text{H}_2\text{O}$ ($\text{A} = \text{Rb}, \text{Cs}$).

$\text{Cs}(\text{UO}_2)(\text{HGeO}_4) \cdot \text{H}_2\text{O}$	$\text{Rb}(\text{UO}_2)(\text{HGeO}_4) \cdot \text{H}_2\text{O}$	Assignments	Ref.
122, 135, 150, 175	106, 123, 179, 195	Mixing modes	14
203, 230, 239, 254, 261, 285, 303,	235, 255, 265, 285, 298,	$\nu_2(\text{UO}_2)^{2+}$	5
330, 378	328, 381		
429	434	$\nu_4(\text{GeO}_4)^{4-}$	15, 16
680	689	$\nu_3(\text{GeO}_4)^{4-}$	15
735, 751, 788	739, 762, 791	$\nu_1(\text{UO}_2)^{2+}$	6, 7
855	857	$\nu_3(\text{UO}_2)^{2+}$	6, 7
1412, 1521	1402	Ge–OH stretching vibrations	17
2871, 2925	2874, 2928	OH stretching vibrations of H_2O	6, 7, 17

* ν_1 – symmetric stretching vibrations; ν_2 – symmetric bending vibrations; ν_3 – antisymmetric stretching vibrations; ν_4 – out-of-plane bending vibrations.

Table S6. Band positions of $\nu_1(\text{UO}_2)^{2+}$ and $\nu_3(\text{UO}_2)^{2+}$ modes in the Raman spectra of the title phases and comparison between the calculated and experimental U=O bond lengths.

Compounds	ν_1 (cm ⁻¹) ¹⁾	Calculated U=O bond lengths (Å)	ν_3 (cm ⁻¹)	Calculated U=O bond lengths (Å)	Average	U=O bond lengths (Å) in crystal structures	Average
K₄(UO₂)₂Si₈O₂₀·4H₂O	781s 751w	1.831 1.864	813sh	1.853	1.849	1.7525 1.8317 1.7923 1.8213 1.7723 1.7877 1.7821 1.8864	1.803
β-K₂(UO₂)Si₄O₁₀	762s 779s	1.852 1.833			1.842	1.800	1.800
Na₆(UO₂)₃(Si₂O₇)₂	742s 719w 761w	1.874 1.902 1.853	827w 898w 924s	1.842 1.786 1.768	1.837	1.822 1.803 1.827	1.817
Rb(UO ₂)(HGeO ₄)·H ₂ O	791s 762w 739w	1.820 1.852 1.878	857w	1.817	1.842	1.774 1.792	1.783
Cs(UO ₂)(HGeO ₄)·H ₂ O	788s 751w 735w	1.823 1.864 1.883	855w	1.819	1.847	1.783 1.784	1.783

s = strong, sh = shoulder, w = weak,

REFERENCE

- (1) Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. The Crystal Chemistry of Hexavalent Uranium: Polyhedron Geometries, Bond-valence Parameters, and Polymerization of Polyhedra. *Can. Mineral.*, **1997**, 35, 1551-1570.
- (2) Brown, I. D.; Altermatt, D. D. Cica Crystallogr. *Acta Crystallogr., Sect. B.*, **1985**, 41, 244–247.
- (3) Brese, N. E.; O'keeffe, M. Bond-Valence Parameters for Solids. *Acta Crystallogr B*, **1991**, 47, 192-197.
- (4) Jin, G. B.; Soderholm, L. Solid-state syntheses and single-crystal characterizations of three tetravalent thorium and uranium silicates. *J. Solid State Chem.*, **2015**, 221, 405-410.
- (5) Plesko, E. P.; Scheetz, B. E.; White, W. B. Infrared Vibrational Characterization and Synthesis of A Family of Hydrous Alkali Uranyl Silicates and Hydrous Uranyl Silicate Minerals. *Am. Mineral.*, **1992**, 77, 431-437.
- (6) Frost, R. L.; Cejka, J.; Weier, M. L.; Martens, W. Molecular Structure of the Uranyl Silicates - A Raman Spectroscopic Study. *J. Raman Spectrosc.*, **2006**, 37, 538-551.
- (7) Frost, R. L.; Cejka, J.; Weier, M. L.; Martens, W.; Kloprogge, J. T. A Raman and Infrared Spectroscopic Study of the Uranyl Silicates - Weeksite, Soddyite and Haiweeite. *Spectrochim. Acta, Part A*, **2006**, 64, 308-315.
- (8) Sharma, S. K.; Mammone J. F.; Nicol, M. F. Raman Investigation of Ring Configurations in Vitreous Silica. *Nature*, **1981**, 292, 140-141.
- (9) Sharma, S. K.; Philpotts, J. A.; Matson, D. W. Ring Distributions in Alkali- and Alkaline-Earth Aluminosilicate Framework Glasses - a Raman-Spectroscopic Study. *J. Non-Cryst. Solids*, **1985**, 71, 403-410.
- (10) Chernorukov, N. G.; Kortikov, V. E. Na[HSi₂O₆]_n·H₂O: Synthesis, Structure, and Properties. *Radiochemistry* **2000**, 42, 229–232.
- (11) Fleet, M. E.; Henderson, G. S. Sodium Trisilicate - a New High-Pressure Silicate Structure (Na₂Si[Si₂O₇]). *Phys. Chem. Miner.*, **1995**, 22, 383-386.
- (12) Xiao, B.; Schlenz, H.; Dellen, J.; Bosbach, D.; Suleimanov, E. V.; Alekseev, E. V. From Two-Dimensional Layers to Three-Dimensional Frameworks: Expanding the Structural Diversity of Uranyl Compounds by Cation-Cation Interactions. *Cryst. Growth Des.*, **2015**, 15, 3775-3784.

- (13) Matkovskii, A. O.; Gevorkyan, S. V.; Povarennykh, A. S.; Sidorenko, G. A.; Tarashchan, A. N. On the bond characteristics of UO in uranyl minerals from IR spectroscopic data. *Miner Sb Lvovskogo Gos Univ im Franko* **1979**, 33, 11–22.
- (14) Vandenborre, M. T.; Michel D.; Ennaciri, A. Vibrational Spectra and Force Fields of Scheelite-type Germanates. *Spectrochim. Acta, Part A*, **1989**, 45, 721-727.
- (15) Achary, S. N.; Errandonea, D.; Santamaria-Perez, D.; Gomis, O.; Patwe, S. J.; Manjon, F. J.; Hernandez, P. R.; Munoz, A.; Tyagi, A. K. Experimental and Theoretical Investigations on Structural and Vibrational Properties of Melilite-Type $\text{Sr}_2\text{ZnGe}_2\text{O}_7$ at High Pressure and Delineation of a High-Pressure Monoclinic Phase. *Inorg. Chem.*, **2015**, 54, 6594-6605.
- (16) Kaindl, R.; Tobbens, D. M.; Penner, S.; Bielz, T.; Soisuwan, S.; Klotzer, B. Quantum Mechanical Calculations of the Vibrational Spectra of Quartz- and Rutile-type GeO_2 . *Phys. Chem. Miner.*, **2012**, 39, 47-55.
- (17) Frost, R. L.; Cejka, J.; Weier, M. L.; Martens, W. N. Raman Spectroscopy Study of Selected Uranophanes. *J. Mol. Struct.*, **2006**, 788, 115-125.